Section A-Research paper

Effective Removal of Ampicillin Antibiotic Residue from Aqueous Solution Using Advanced Oxidation Process

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Abstract— Hospital sewage is one of the important sources of discharge of antibiotic residue in environment. When disposed improperly, antibiotics can cause complex impacts on environment, such as development of antimicrobial resistance. It is necessary to remove such antibiotic residues from the hospital sewage. Considering this fact, the present work was carried out to evaluate the possibility of applying advanced oxidation processes for removal of ampicillin antibiotic residue from aqueous solution. The different parameters that affect the advanced oxidation process for antibiotic residue from solution were studied by using two different combinations, Hydrogen peroxide with UV radiations and Zinc oxide with UV radiations. The parameters taken for consideration were pH, reaction time and dosage of Hydrogen peroxide and Zinc oxide. The optimal conditions for removal of ampicillin were found to be0.5 ml of hydrogen peroxide and zinc oxide per 100 ml, reaction time 120 min for both the treatments and pH 4 and 10 for H_2O_2/UV and ZnO/UV treatment respectively. Chemical Oxygen Demands (COD), before and after oxidation process was determined to ensure removal of antibiotic residue from their aqueous solution. The experimental results indicated that advanced oxidation process successfully achieved very good removal efficiency and it can be used for pretreatment of ampicillin containing wastewater.

Keywords: Ampicillin, COD, Hydrogen peroxide, Zinc oxide, UV radiation.

I. INTRODUCTION

Antibiotics and pharmaceuticals both are used to treat infections and indirectly to improve public health as well as quality of life [1]. Among all the pharmaceutical drugs that cause contamination of the environment, antibiotics have an important place due to their high consumption in both veterinary and human medicines. The presence of antibiotic residues at low concentration in the environment is responsible for development of antimicrobial resistance (AMR) [2]. Such microorganism adds toxic effects on living system. The effects are found not only on algae and crustaceans in higher concentration but chronic effects have also been observed at lower concentrations [3]. The incidences of development of AMR have increased day by day and it has been seen that this increase is due to the excessive use of antibiotics and their disposal [4]. Number of antibiotics and AMR have been reported in diverse environment such as aquaculture [5], livestock farming [6], hospital wastewater [7] and domestic sewage [8].When hospital wastewaters disposed in water bodies it get contaminated with antibiotic residues. It is suspected that the antibiotic residue occurrence accelerates resistance spread in the environment [9]. Therefore AMR is an emerging global threat [10] and antibiotic residue are being considered as public health hazard [11]. It has been observed that antibiotic residues are present in drinking water [12], wastewater treatment plants, soil, surface waters, ground waters [13]. Both narrow and broad spectrum antibiotics are detected globally in various environmental samples [14]. Even low concentration of antibiotic in the aquatic ecosystem is a great challenge for water quality due to their toxic impact on non-targeted organisms [15]. So, it is important to remove these contaminants from wastewater. There are several methods available which have shown the possibilities of antibiotic removal are adsorption, bioelectrochemical, hydrolysis, redox reactions and photolysis [16].

Ampicillin ($C_{16}H_{18}N_3NaO_4S$) has extended spectrum penicillin effective against gram positive as well as gram negative microorganisms [17]. It has been used in the treatment of enteric fever, respiratory tract infections, urinary tract infections, skin and soft tissue infections [18]. Owing to the improper treatment of pharmaceutical wastewater, its excessive use in food additives for livestock breeding or animal husbandry and incomplete metabolism in human and animal bodies, excessive antibiotics are discharged into the environment [19]. The conventional biological wastewater treatments are not appropriate for antibiotic removal due to their toxic effects on microorganisms [20]. Therefore, cost effective methods for commonly used antibiotic removal from wastewater are urgently needed.

Advanced Oxidation Processes (AOP's) are the most attractive and favorable methods for the effective removal of organic pollutants in wastewater [21]. These methods are based on the in situ generations of strong oxidants that are hydroxyl radicals for oxidation of organic pollutants [22]. Generation of OH radicals in aqueous solution is more effective which a result of "Advanced oxidation process" there is several methods are available for generation of OH radicals. Combined use of UV radiation with H_2O_2 and zinc oxide are some of them [22]. H_2O_2 with UV radiation and ZnO with UV radiation are used as strong oxidizing agents.

H_2O_2 is a high potential redox reagent and has a number of unique properties such as water solubility and non-toxicity. Its use does not involve formation of any hazardous waste because its decomposition products are only water and oxygen [23]. H_2O_2 has number of advantages including ability to use it in a wide range of temperature and pH, high selectivity of oxidation of various wastewater impurities, high stability of commodity solution during storage, simplicity of hardware design of water purification process and ecological compatibility [24]. It is well known that hydrogen peroxide is used in oxidation of hydrogen sulfide, sulfides, thiosulfates, sulfites, nitrogen compounds, chlorine compounds and cyanides. An advantage of H_2O_2 use in water treatment has significance as it does not cause secondary water pollution by decomposition products. The substances formed as a result of chemical processes are less dangerous than their reactants [25]. H_2O_2 can be used alone or with a catalyst such as iron, UV light, Ozone, catalytic autoxidation and many more [26]. (Ksibi, 2006).

Some semiconductors, including ZnO when illuminated by photons having an energy level that exceeds their bond gap energy excites electrons (e^-) from the valence bond and holes (h+) are produced. The generated valence bond holes react with water or hydroxyl ions adsorbed on the catalysts surface to generate hydroxyl radicals which are strong oxidants [27]. There are many reported studies using ZnO as catalyst in photocatalytic degradation of organic pollutants [28].

UV light is helpful to form more hydroxyl free radicals [25]. Organic substances are generally more sensitive to light than inorganic substances and hence are subjected to degradation by absorption of photons of hard UV radiation which forms hydroxyl radicals which plays leading role in degradation of organic matter. These hydroxyl radicals in aqueous solution are more effective as a result of Advanced Oxidation Process [29].

Use of H_2O_2 and UV radiation for the degradation of organic compounds

The direct photolysis of H_2O_2 leads to the formation of OH radicals [30].

$$\mathrm{H2O2} \overset{h\nu}{\rightarrow} 2OH$$

Conversion of unwanted compounds can take place by absorption of UV light (photolysis) or reaction with hydroxyl radicals [29]. $Compound + OH \overset{h\nu}{\rightarrow} degradation\ compound + CO2 + H2O$

Some compounds may even be mineralized towards CO_2 and H_2O [25]. Completion of oxidation reactions, as well as oxidative destruction of compounds immune to unassisted H_2O_2 oxidation, can be achieved by supplementing the reaction with UV radiation [29].

Use of ZnO and UV radiation for the degradation of organic compounds

Reactions (1) to (3) show the formation of hydroxyl radicals by photo catalytic process [31].

$$ZnO + h\nu \rightarrow ZnO\ (e- \ + h+) \qquad (1)$$

$$h+ \ + H2O \ \rightarrow H+ \ + \cdot OH \qquad (2)$$

$$h + +OH- \rightarrow \cdot OH \qquad (3)$$

During the present study, attempt has been done to oxidize the antibiotic residue of ampicillin through standard aqueous solution in presence of UV light by using two different combination of advanced oxidation process those are $H_2O_2$and zinc oxide. The degradability of antibiotic residue was assessed by Chemical Oxygen Demand (COD) analysis, as COD is measure of oxygen equivalent of the organic matter in water sample [32].

MATERIAL AND METHODOLOGY

Chemicals and antibiotics used for the experiment

Analytical grade hydrogen peroxide (H_2O_2) 30 % (W/W), ampicillin sodium salt and zinc oxide was purchased from HI Media. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from Qualigens Fine Chemicals Pvt. Ltd.

Preparation of aqueous solution of ampicillin

Standard antibiotic aqueous solution of 100 mg/l was freshly prepared in double distilled water and stored at 4 ͦC for further use.

Experimental Procedure

Experiment was carried out by using Batch method [33]. Effect of various parameters such as reaction time, pH and dosage of photo catalyst on COD reduction efficiency was studied. In the batch method, 100 ml. aliquot of the ampicillin solution of known concentration were agitated with dosage of H_2O_2 and ZnO varying from 0.1 ml. to 0.6 ml. A reaction time of 30 min to 120 min was provided. pH was adjusted using 1 N H_2SO_4 and 1N NaOH. Thereafter, the mixture was subjected to UV radiation with wavelength 354 nm. After completion of preselected time samples were taken out and filtered through Whatman no. 42 filter paper for COD determination.

COD reduction efficiency

Chemical oxygen demand was determined as per the standard closed reflux titration method. To reduce interference of H_2O_2 in COD determination, pH was increased >10 to decompose H_2O_2 to oxygen and water. pH measurements were done through a pH meter.

COD reduction efficiency was calculated by using following formula [34].

$$\textbf{COD reduction efficiency}\ (\%) = \frac{Co - Cf}{Co} \text{X } 100$$

Where,

Co= initial COD reading

Cf= final COD reading

II. RESULT AND DISCUSSION

The experiment was carried out to investigate the ability of H_2O_2 and ZnO to work as oxidant at various pH and time intervals. This oxidative property was analyzed through COD reduction efficiency which further indicates the degradation of antibiotic that is ampicillin. Treatment to the aqueous solution having concentration 100 mg/l was conducted using oxidation process (UV and H_2O_2) and (UV and ZnO) at room temperature under different operating conditions as initial H_2O_2 and zinc oxide concentration, pH and contact time in order to examine optimum conditions. The efficiency of these photochemical methods was determined by monitoring COD which is commonly used to monitor performance of conventional wastewater treatments. COD reduction indicates the degradation of organic compounds contained in water to be treated.

Effect of agitation time on COD removal rate

If the fixed retention time is too short, the intermediates remaining in solution could nevertheless be structurally similar to the initial compounds and therefore, no degradable [35]. The photolysis reaction takes place when chemical substances absorb light. The degradation of antibiotic is due to hydrolysis and such reaction proceeds through the attack of nucleophile H_2O to the beta lactam ring followed by ring opening [36]. The efficiency of the oxidation process depends upon the formation and scavenging of the hydroxyl radical which vary with respect to the organic compound and irradiation time provided [37].

To consider the effect of time on Chemical Oxygen Demand removal efficiency (%) of antibiotic, the H_2O_2 and ZnO concentration and time were made variable. Fig. 1 and 2 represents a typical reaction curve showing the rate of % reduction of COD with reaction time. By H_2O_2 and ZnO dosage varying from 0.1 ml to 0.5 ml, time kept varied from 30 min to 150 min. The results showed that antibiotic degradation in terms of COD removal increases with retention time for both the treatments.

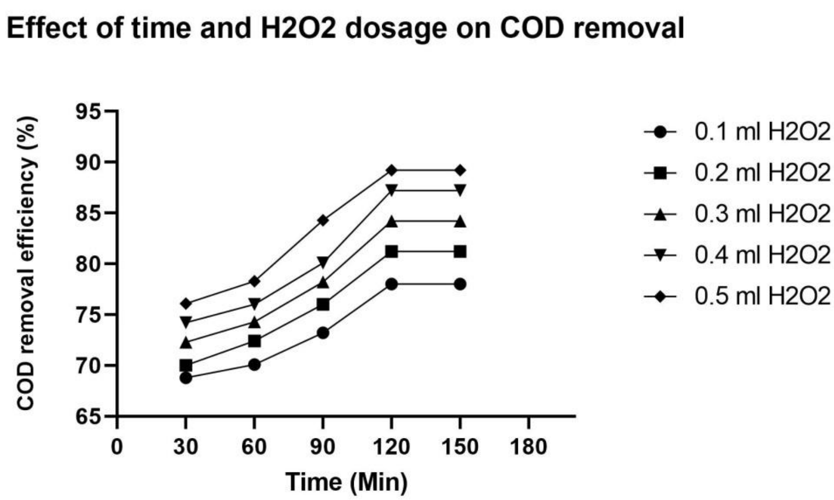

Figure 1: Effect of time and H_2O_2 dosage on COD removal

As per the obtained results for H_2O_2 and UV treatment, more COD reduction occurred after 60 minutes of oxidation reaction. COD removal rate was about 68 to 90.3 % after 120 min at different dosage of H_2O_2. For further increase in time up to 120 min there was no increase in the COD reduction and reduction efficiency remain stable once it reaches to equilibrium.

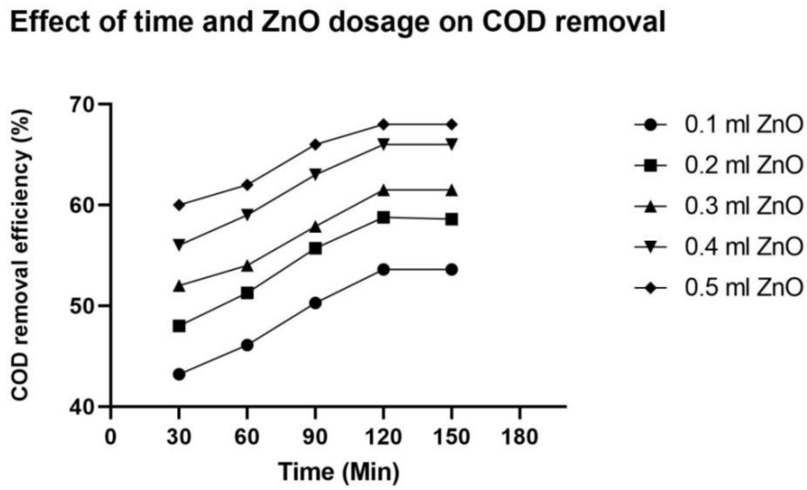

Figure 2: Effect of time and ZnO dosage on COD removal

As per the obtained results for ZnO and UV treatment removal rate was about 43 to 68 % after 60 min at different dosage of zinc oxide. After 120 minutes there was no increase in the COD reduction and the efficiency remain stable once it reaches to equilibrium.

In both the treatments it is observed that COD removal % increases with respect to agitation time. It is clearly evident from (Fig.1 & 2) that removal efficiency increased rapidly with agitation time and then remains stable after achieving equilibrium time.

Effect of catalyst dosage on COD reduction

To observe the effect of H_2O_2 and ZnO dosage as catalyst, dosage of both were varied from 0.1 to 0.6 ml for 100 ml of ampicillin antibiotic aliquot.

H2O2 dosage can play significant role in Advanced Oxidation Process as it is main component that limits the production of hydroxyl radicals during treatment by UV and H_2O_2 [38]. Concentration of H_2O_2 plays significant role in efficiency of entire degradation process [39]. It has been observed during experiment that during the COD of the solution decreases with the increasing concentration of H_2O_2. However excessive concentration of the H_2O_2 can lead to an increase in the COD of the effluent, in addition to reaction with hydroxyl radicals it form hydroperoxyl radicals, a species with lower oxidizing power when compared with hydroxyl radicals who are having high oxidizing power [40]. Generally it has been found that the percentage degradation of contaminants increases with respect to dosage of H_2O_2 [41]. However, the unutilized H_2O_2 during the process contributes to rise in COD. The care should be taken in the selection of operating concentration of H_2O_2 [39]. When more than optimum dose of H_2O_2 is added then there will be increase in COD level due to presence of residual H_2O_2 remains in the treated solution [42]. The presence of H_2O_2 is harmful to living biota [43].

However at excessive H_2O_2 concentration, the reaction rate decreases and sometimes is negatively affects the progressive increase in concentration of H_2O_2. This is might be due to the auto decomposition of H_2O_2 to oxygen, water and scavenging of hydroxyl radicals by H_2O_2 [44]. Excess H_2O_2 reacts with hydroxyl radicals competing with the organic pollutants and consequently reducing the efficiency of the treatment, the H_2O_2 itself contributes to the scavenging hydroxyl radicals [45]. Higher concentration of H_2O_2 means a higher production of hydroxyl radicals even though excessive H_2O_2 favors the occurrences of auto scavenging effect. Therefore, H_2O_2 should be added at an optimal concentration to achieve the high efficiency for degradation process.

The obtained results shows that at constant retention time (30 min to 150 min), increase in dosage of H_2O_2 it leads to increase in % reduction of COD which is 68 % at 0.1 ml dose to 90% at 0.5 ml at 0.6 ml it has been found that results are negatively affected. Therefore, the optimal H_2O_2 dose is 0.5 ml per 100 ml of solution to be treated. For 0.5 ml dose the results have shown the 80-90 % that is highest efficiency for COD removal as shown in Table no. 1.

Table 1: Effect of H_2O_2 dosage in COD reduction

COD reduction efficiency in % at variable time and H2O2 dosage					
H2O2 Concentration in ml	**30 min**	**60 min**	**90 min**	**120 min**	**150 min**
0.1	68.79±0.3	70.1 ±0.1	73.2 ±0.2	78 ±0.15	79 ±0.2
0.2	70±0.2	72.4 ±0.1	76 ±0.2	81.2 ±0.2	82.3±0.1
0.3	72.3±0.2	74.3±0.2	78.2±0.2	84.2±0.1	85.2±0.2
0.4	74.2±0.1	76±0.2	80.1±0.1	87.2±0.2	88.2±0.2
0.5	76.1±0.1	78.3±0.3	84.3±0.3	89.2±0.2	90.3±0.3
0.6	44.3±0.3	44.9±0.1	45.6±0.2	46.1±0.1	46.2±0.3

Zinc oxide can absorb a larger fraction of the solar spectrum than other TiO_2. Hence ZnO photocatalyst is considered more suitable for photocatalytic degradation [46]. It is seen that degradation of antibiotics increased with ZnO concentration is possible due to the increase of hydroxyl radical formation. Increasing ZnO concentration above 0.5 g/L did not show any significant progress in antibiotic degradation [27]. It is seen that the degradation of Amoxicillin, Diclofenac and Paracetamol can be done by solar advanced oxidation and observed a positive effect on the degradation efficiency when increasing its concentration [47]. The increased degradation is due to the increase of total surface area and number of active sites of the photo catalysts available for photo catalytic reaction when increasing the dosage [48].

The obtained results from ZnO and UV irradiation treatment shows that at a constant retention time (30 min to 150 min) while increasing the dosage of zinc oxide increase in the % reduction of COD from 42 % at 0.1 ml dose to 68 % at 0.5 ml it has been seen that at 0.6 ml the results remained unaffected. This presumably due to the decreasing UV light penetration as a result of increasing turbidity and thus decreasing the photo activated volume of suspension [31]. Therefore, the optimal ZnO dose is 0.5 ml per 100 ml of solution to be treated. For 0.5 ml dose the results have shown the 53 - 68 % efficiency for COD removal as shown in Table no. 2.

Table 2: Effect of ZnO dosage on COD reduction

COD reduction efficiency in % at variable time and zinc oxide dosage					
ZnO dosage in ml	**30 min**	**60 min**	**90 min**	**120 min**	**150 min**
0.1	43.2 ± 0.1	46.1 ± 0.2	50.3 ± 0.3	53.6 ± 0.2	53.6 ± 0.2
0.2	48 ± 0.3	51.3 ± 0.1	55.7 ± 0.2	58.8 ± 0.1	58.6 ± 0.2
0.3	52 ± 0.1	54 ± 0.2	57.9 ± 0.3	61.5 ± 0.2	61 ± 0.1
0.4	56 ± 0.1	59 ± 0.3	63 ± 0.1	66 ± 0.1	66 ± 0.2
0.5	60 ± 0.2	62 ± 0.1	66 ± 0.2	68 ± 0.3	68 ± 0.1
0.6	60 ± 0.2	62 ± 0.1	66 ± 0.2	68 ± 0.3	68 ± 0.1

In both the treatments it is observed that antibiotic degradation in terms of COD removal increases with respect to dosage of catalyst. After reaching to the certain dosage it is found that efficiency is negatively affected in case of H_2O_2 and UV treatment. It is remained unaffected in case of ZnO and UV treatment.

The effect of pH

The pH value has an effect on the oxidation potential of hydroxyl radicals because of the reciprocal relation of the oxidation potential to the pH value [35]. The pH value influences the generation of hydroxyl radicals and hence the oxidation efficiency [27]. To determine the optimum pH, experiment were conducted by varying the pH in the range 2-10. The experimental conditions were 100 ml ampicillin stock solution of 100 mg/l, initial COD 400 mg/l, retention time of 120 min and H_2O_2 dosage was 0.5 ml for both combinations of advanced oxidation process.

For H_2O_2 and UV treatment maximum COD reduction was achieved at pH 4 by keeping constant H_2O_2 dose at 0.5 ml. for 120 min. It was seen increase in pH substantially decrease the efficiency of COD reduction. It is due to hydroxyl radicals formed, which reacts more slowly with H_2O_2 and therefore, the degradation of H_2O_2 is slow, the scavenging effect of hydroxyl radical by H^+ becomes significant at very low ranges of pH [49]. According to the reaction the ions of H^+ may have inhibited the generation of hydroxyl and per-hydroxyl radicals that were necessary to achieve the oxidation process [50].

$$HO^* + H^+ + e^- \longrightarrow H_2O$$ [50].

At pH value greater than 7, a rapid decrease in COD reduction was also observed. This is due to rise in pH which makes the solution alkaline. As H_2O_2 is unstable in alkaline condition decomposes to give O_2 and H_2O. Also consequently losses its oxidizing capacity [51]. In an acidic condition, at pH 5.0, as the photocatalyst has negative charge on it while ampicillin has a positive charge on it, which makes the degradation more and efficient [52]. The degradation and mineralization efficiency of organic substances by use of UV and H_2O_2 depends importantly on pH in terms of degradation and mineralization [53]. There was no consistency about pH range and it was found that optimal pH range changes from one case to another [54]. Efficiency of UV and H_2O_2 in treating olive mill wastewater was independent of initial pH range but best results for treatment of pulp and paper mill wastewater by this process was achieved in alkaline condition [55]. An optimal pH of 5 was found during UV and H_2O_2 treatment of pharmaceutical wastewater [53]. The findings of current work shown in Graph No. 1 are in line with previous study which recommends that the optimum level of pH for oxidation is not dependent on nature of wastewater which ranges in between 3-5 pH [42].

For Zinc oxide and UV radiation treatment maximum COD reduction was achieved at pH 10. Result shows the effect of pH on antibiotic degradation in terms of COD removal. High degradation of antibiotic in alkaline condition may be due to two facts. First is the presence of large quantities of OH- ions on ZnO surface favoring formation of OH radicals [56]. Second is the hydrolysis of the antibiotic due to instability of beta lactam ring at high pH [57].

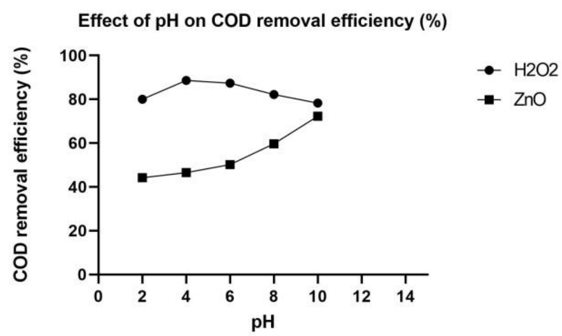

Figure 3: Effect of pH on COD removal

From Fig.3 it is clearly seen that effective pH for H_2O_2 and UV irradiation treatment lies in acidic condition as pH 4 has shown highest degradation in terms of COD removal in %. While effective pH for zinc oxide and UV irradiation treatment pH range lies in alkaline condition as pH 10 has shown highest degradation for ampicillin in terms of COD removal in %. Obtained results represents that the COD reduction in advanced oxidation method by combination of H_2O_2-UV and ZnO-UV are affected by pH.

One way ANOVA:

A statistical (one-way ANOVA) performed on the results at a 5 % level of significance indicated that Ampicillin degradation were significantly affected by pH, H_2O_2 and ZnO (Table 3).

Table 3 One-way ANOVA for Ampicillin degradation at different H2O2, ZnO Concentration and pH.

Parameter	**No. of Groups**	**Antibiotic**	***Sum of square (SS)***	***Degree of Freedom (df)***	***Mean Square (MS)***	***F***	***P-value***	***F crit***
H_2O_2	6	Ampicillin	1015.484817	5	203.0969633	7.428061	0.000247	2.620654
ZnO	6	Ampicillin	961.6266667	5	192.3253333	10.76177	0.000555	2.620654
pH	2	Ampicillin	2062.096	1	2062.096	26.84898	0.000841	5.317655

P-value 0.05 (>0.05) = statistically insignificant, *P-value* 0.05 (<0.05) = statistically significant. Ho = null hypothesis, which states that there is no difference between the mean of all groups. H1 = alternative hypothesis, which states that there is difference between mean of all groups. When F statistical > F critical value, then the test is significant. Therefore, for all three parameters decision is to accept alternative hypothesis and reject null hypothesis.

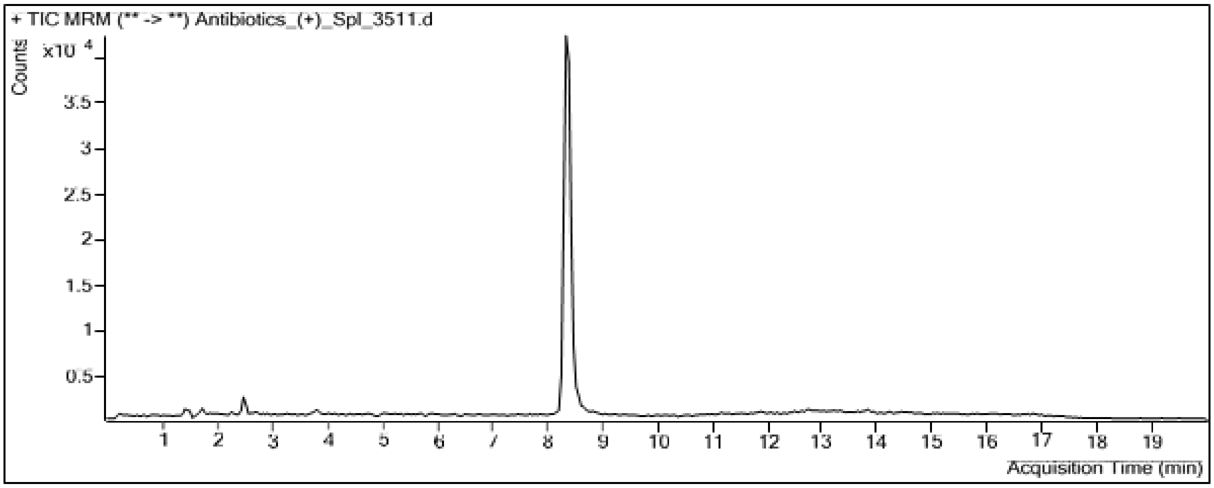

Figure 4: Chromatogram of Ampicillin using LC-MS/MS

III. CONCLUSION

In present study, advanced oxidation method using two combinations H_2O_2-UV and ZnO-UV for degradation of Ampicillin from aqueous solution in terms of COD removal was investigated. The reaction parameters such as time, pH, amount of H_2O_2 and ZnO, were examined using batch method at room temperature and COD removal rate as a standard for assessing. Result shows that the treatment of ampicillin aqueous solution by H_2O_2/UV and ZnO-UV treatments are efficient as it has achieved 90 % and 68 % COD reduction efficiency respectively. As compare to ZnO-UV, H_2O_2-UV shown high percentage reduction of COD. The influences of operating conditions on the efficiency of both treatment methods were evaluated. It is found that degradation rate of ampicillin increases with increasing time and 120 min is the optimal retention period for treatment for both treatments. It is also observed that with increasing dosage of H_2O_2 and ZnO efficiency of treatment increases up to certain concentration, after reaching to the equilibrium it remains constant. Optimal H_2O_2 and ZnO concentration is 0.5ml/100ml of solution. The optimal initial pH is 4 and 10 for H_2O_2-UV and ZnO-UV treatment respectively. One way ANOVA shows that ampicillin degradation significantly affected by all three parameters. From obtained results it can be concluded that advanced oxidation by H_2O_2-

UV and ZnO-UV are highly efficient, cost effective, eco-friendly and it can be implemented to the wastewater treatment plants containing ampicillin residue.

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